

TRIBOLOGICAL BEHAVIOR OF Ni-P ELECTROLESS PLATING OF LOW ALLOY STEEL WITH CARBON NANO TUBES

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ABSTRACT

The basic aim to study wear resistance and hardness of heat treatment of coatings with electroless Ni-P-CNT. Various concentration of CNTs range, 0, 0.1, 0.2 and 0.4 g/L in Ni-P-CNT composite was deposit on low alloy steel in electroless immersion. The Ni-P-CNT electroless coatings were prepared by using nickel chloride as a source for nickel in alkaline bath and used CNT. The formulas were characterized with means of EDS, SEM, micro hardness, surface roughness and wear resistance measurements. The results of that micro hardness showed higher hardness (560 HV) was achieved for heat-treated sample (Ni-B-0.1g/l CNT). The results enhance the concentration of CNTs caused structure of as-coated Ni-P conversion from amorphous to crystalline. Compared to the Ni-P coating, wear resistance of composite coating (Ni-P-CNT) is better, and they become much better with the increase of CNT concentration. The adding of CNT makes the coating denser and the presence of CNT makes the size of grain to decrease in accordance with the heat treated formulae, but too much CNT deposited on the substrate leads to a high region of the CNT wrapped together. and agglomeration that occurs is very unfavorable to coating, resulting in lead wear resistance of the composite coating and becomes worse.

KEYWORDS: Electroless Ni-P-CNT Coating, Micro Hardness & Wear Resistance

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1.INTRODUCTION

In the recent years, electrical and electronics engineering have faced the problem of how to coat dielectrics (ceramics, polymers) and semiconductors. Certain metals are difficult to be coated, such as titanium, aluminum, tungsten, molybdenum and magnesium alloys.¹

Coating materials to resist corrosion is an effective way to protect against corrosion and wear. Coating layer must have a suitable thickness to make them able to isolate all the reactants from each other. There are different types of coating, including metallic plating, which includes electroplating and electroless coating. The known way is the immersion in molten metal and the method of spraying minerals in addition to non-metallic plating [2].

The electroplating is defined as the deposition of product layer on a surface of metal and that treatment is worked with the technique of an electrolytic. It contains the electrolyte solution for metal liquefied salt required to be deposited, contains the electroplating cell – an anode. On the surface of the anode, oxidation process occurs. The other cathode, in reduction of the cathode surface of the positive ions occurs and represents the electrolyte-conducting medium. The electric current movement through the electrolyte is connected with the flow of material and also a salt that enables conductivity of the solution.³

Plating electroless of Ni-P alloy technique is a well-known commercial treatment and has applications in several fields because very good properties such as large corrosion resistance, large wear resistance, large hardness and excellent ductility. Electroless coating is a technique of coating metal by chemical rather than electrical means. It is beneficial because it allows the coating of metals and plastics by a process of controlled autocatalytic, or self-continuing reduction. Chemical reaction reduction with the controlled chemistry coating and electroless has developed as the regions' growth in metal finishing, surface engineering, etc., and is likely to grow at a rate beyond 15% per annum, certainly no other chemistry is growing at this rate. Electroless coatings have mechanical and physicochemical properties, which are being used increasingly.⁴

The advantages for this technique is regularity of the thickness of the coating layer even on parts with complex and small shapes, which is one of the main difficulties in electroplating due to weak ionic strength for electroplating, as coating layers are generally devoid of porosity, which prevents the entry into force of ions and reduce the corrosion process. For these technical features, as the microstructure of the layers of coating, change crystalline and deposit the chemical compounds by heat treatment to improve resistance to corrosive environments.⁵

Improved of mechanical properties, resistance of wear and nano composite coatings have large attention. Nanocomposite coating have other appropriate and identified solid lubricants like MoS₂,⁶ PTFE⁷ and CNT⁸, which can act to decrement in the friction coefficient and also enhance the wear resistance on the surface. Because of the great tensile strength of carbon nanotubes with elastic modulus⁹, make it widely used in ceramic composites and metallic composites such as Cu-CNT¹⁰ and ZrO₂-CNT¹¹. Treatments of mechanical process of chemical treatment, including used surfactants of the CNT and ball-milling are the more general processes used to treat their bad dispersion issue^{12,13}].

Recently, carbon nanotubes (CNT) are co-deposited in Ni-P matrix and their tribological properties are evaluated. Carbon nanotubes are the most typical one-dimensional nanomaterial (in order of micrometers in length and nanometers in diameter), which possess unique topological hollow tubular structure¹³. CNT has many potential and practical applications due to their outstanding electrical and physical properties. The Ni - P-CNT composite coatings are successfully fabricated by suspension of CNT in an electroless bath. Ni-P-CNT (CNT = 12 vol.%) and exhibit better wear resistance than that of Ni-P-SiC and Ni-P-graphite, in both as-plated and heat-treated conditions. Ni-P-CNT provides a low coefficient of friction with significantly improved electrochemical characteristics. CNTs can be impregnated into very small pores in the porous Ni-matrix to make the passive film more stable and compact because of that it shows excellent corrosion resistance and high microhardness. Ni-P-CNT composite coatings have wide applications in modern electronic industry.¹³

Formation of a metastable equilibrium phase and precipitation of Ni₃P compound is primarily responsible for the improvement in abrasive wear behavior of the nanocrystalline coatings with heat treatment temperatures. At higher thermal treatments, a change in the deformation mechanism (Orowan mechanism) determined by the coarsening of Ni₃P precipitates, is associated with the decrease in abrasive wear resistance of the coatings.¹⁴⁻¹⁶

The aim of this study is to explain effects behavior of electroless. Ni-P-CNT coating with various concentrations of CNT and heat treatment coating on some mechanical properties (microhardness and roughness), resistance of wear and microstructure of low alloy steel.

2. EXPERIMENTAL

2.1. Preparation of Substrate

Substrate metal used in this work was low alloy steel. Specimens (20 mm diameter \times 10 mm height) were used as the substrates. The chemical analysis for this alloy and details composition (weight %) is shown in table 1.

Table 1: Chemical Compositions of Low Alloy Steel

Element	C	Si	Mn	Al	Cu
W%	0.311	1.12	1.17	0.0084	0.076

All specimens were grinded and polished as ASTM by emery paper (tungsten oxide paper) no. (180–2000), then samples were washed by distilled water and ethanol and dried by using an electrical dryer. Polishing was conducted by diamond paste, specimens were immersed in acetone for 30 min. Before coating, specimens were immersed in solution including materials (30 g/L NaOH, 60 g/L NaCO₃ and 60 g/L NaPbO₄ for one-minute period at 60°C temperature moving the electrolyte using magnetic stirring by supply power (5 volts) to remove oil and any dust from metal surface. After that, the specimens were washed with distilled water, after that it directed immersion in coating solution

2.2 CNT Ball-Milling

MWCNT with purity more than 95%, 10–30 μ m with length 5–10 nm in inside diameter and 20–30 nm with outside diameter. For to enhance dispersion for CNT in electroless coating bath, as-received CNT were ball milled at 3 hours using machine of planetary ball-mill with balls of steel with various diameters have been used for mix CNT in cylindrical stainless steel jar, rotating speed and then (10-min) fracture intermitting each (20 min) of milling to reduce heat build-up. Ethyl alcohol has been used in wet mixing.

Figure 1 shows Field Emission Scanning Electron Microscopy in MIRA3 TESCAN Company in Iran, images of ball milled and as-received CNT. The image shows ball-milled CNT are smaller and the most straight, so to enhance dispersion for CNT at bath of electroless.

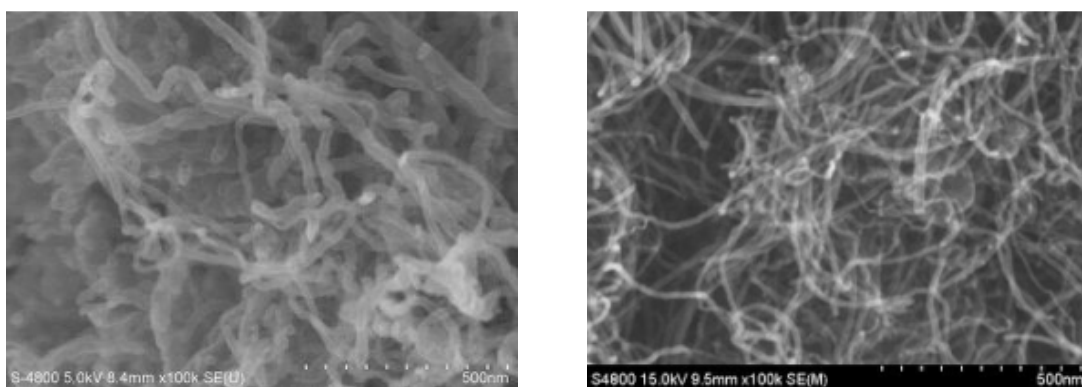


Figure 1: FESEM Images of (a) as-Received CNT and (b) Ball-Milled CNT

In order to disperse uniformly carbon nanotubes in electroless Ni-P coatings and no agglomeration to provide stable and homogenous dispersion in the metallic matrix phase should use surfactants (sodium dodecyl sulfate (SDS) with CNT and mixed together with water by ultrasonic device for 45 min.

2.3 Electroless Bath Preparation

After completion of preparing surfaces for coating, electroless bath were prepared for the process according to concentrations shown in table 2. The coating Ni-P was deposited on low alloy steel with electroless plating process. Value

of PH, the plating bath was varied between (8 and 10). The electroless coating of Ni-B was performed at $95 \pm 2^\circ\text{C}$ for 60 min. Through coating, solution of bath are agitated by a magnetic stir to avoid localized overheating and reduce the fluctuation of ionic concentration. The coating process, for Ni-P-CNT deposition by changes of concentration for CNT (0, 0.1, 0.2, 0.4 g/l CNT). Firstly, CNTs were dispersed in the ultrasonic bath, then addition of CNT to the Ni-P prepared bath. Figure 2 shows the experimental setup for the electroless composite deposition. After the completion of the process of coating, specimens were placed inside a vacuum oven to dry for 30 minutes, at a temperature of 50°C .

Table 2: Operating Conditions for Electroless Bath

Bath Composition	g/L
Nickel chloride. ($\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$)	30
Sodium hypophosphite (NaH_2PO_2)	10
Amina chloride	50
Sodium citrate	84
Sodium Dodecyl Sulfate (SDS)	0.2
Carbon nanotube(CNT)	0, 0.1, 0.2, 0.4
Operating conditions	
pH	(8-10).
Temperature	95°C
Time	1 HR

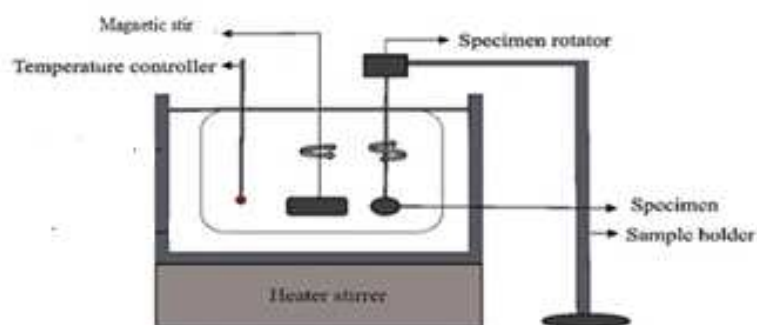


Figure 2: Setup of Experimental Electro Less Deposition.

2.4 Heat Treatment

In this work, annealing process is conducted in furnace-coated specimens, which were soaked at a temperature (400°C) for a period of one hour. Then, specimens were furnace cooled at room temperature.

2.5 Characterization

Micro hardness of the coating layers were measured by using (TH-717 Vickers hardness tester), a load of 25 g was applied for 15 sec. Three readings were recorded for each specimen coated and one at the substrate. Test of wear is performed at room temperature (25°C) and at a relative humidity of 40%. The used load was 10 N. Velocity of sliding is (0.1 m/s) and distance of sliding is (500 m). The disc was carbide steel. A sensitive scale weighs the specimens before and after the wear test to calculate the mass loss of coatings. The specific wear rate of the specimen is calculated (ASTM G99) using ($W_s = \Delta w / \rho F S$), any (W_s) is specific wear rate, (Δw) is weight loss of specimen, (ρ) is the density, (F) is normal load (N) and (S) is distance of the sliding (m).

Then, the average value was taken. The value of measurement for surface roughness was completed for the coated samples before and after heat treatment using a common parameter Ra in μm , surface roughness Test (HER210 Model) was used to calculate Ra with an accuracy of $0.05 \mu\text{m}$ and the mean of 10 measurements was recorded. Examination of coatings to crystalline phase identification of coating phase is by EQUINOX X-3000, by Cu K α ($\lambda=1.54187\text{\AA}$) radiation and scanning domain of 2θ between 5° and 118° , worked on 40kV and 30mA is used for identification of samples crystal structure

3. RESULTS AND DISCUSSIONS

3.1 Scanning Electronic Microscope (SEM)

Figure 3 expresses the cross-sectional surface coating Ni-P-0.1g/l CNT and thickness of coating ($5.02 \mu\text{m}$). It was treated at 400°C for 1 hour.

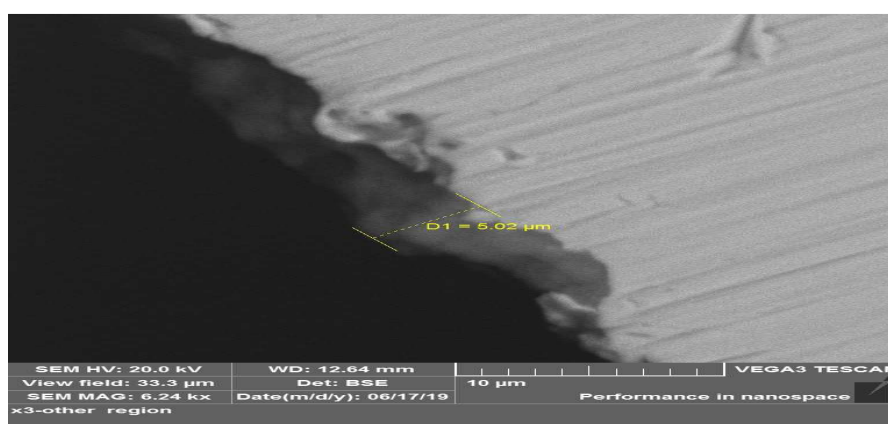


Figure 3: SEM Of Ni-P –CNT Coating of Surface of Cross Section of Heat Treatment Specimens.

The SEM study that was performed on the agglomerates reveals that they are composed of the particles. Figure 4 expresses the morphology of the CNT embedded in Ni-P matrix and the CNT precipitates. They are of irregular shapes. They act as reinforcement particles in Ni-P coatings. In addition, CNT appears in the coatings, which contain CNT particles. The coatings composite expresses a structure of spherical nodule by good uniformity and coverage of dense.

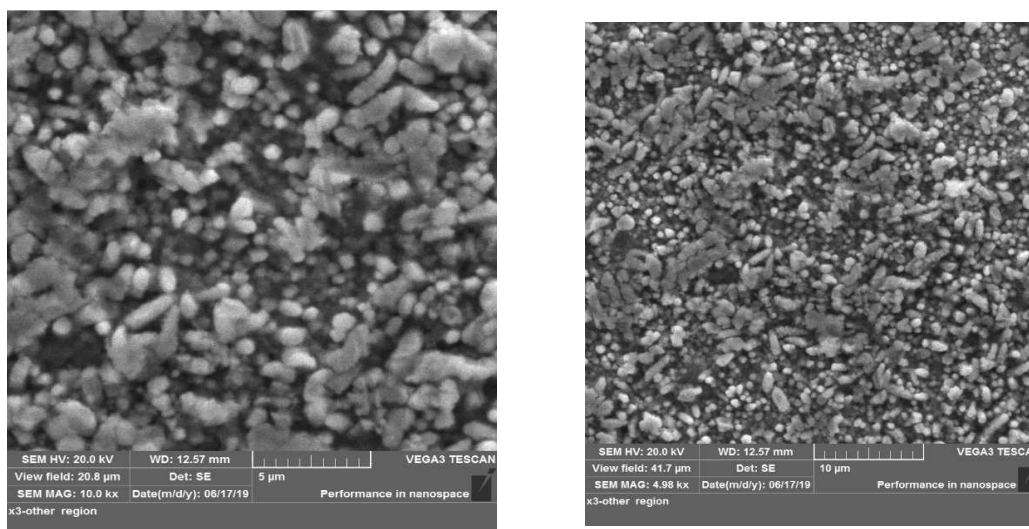


Figure 4: SEM of Ni-P-CNT at (a) (4980 X) Magnification and (b) (10000 X) Magnification.

3.2 EDS Characterization

Figure 5 shows the EDS of Ni-P-CNT composite electroless coatings at the required parameters of the process that indicates that the coating contains 80% Ni, 10.5% P and 0.1% CNT (mass fraction), which gives exactly the initial amount of 10.5% P when the percentage of P is higher. 10% of the structure of the coating is expected to be amorphous. This is exactly what happened.

The phosphorus content indicates that the coating is a type of coating high phosphorus. This result is supported by the SEM metallography. Figure 5 high incorporation of CNT particles in composite coatings can be ascribed to the smaller size of the particles¹⁷ these particles are believed to be swept away from the electrode surface.

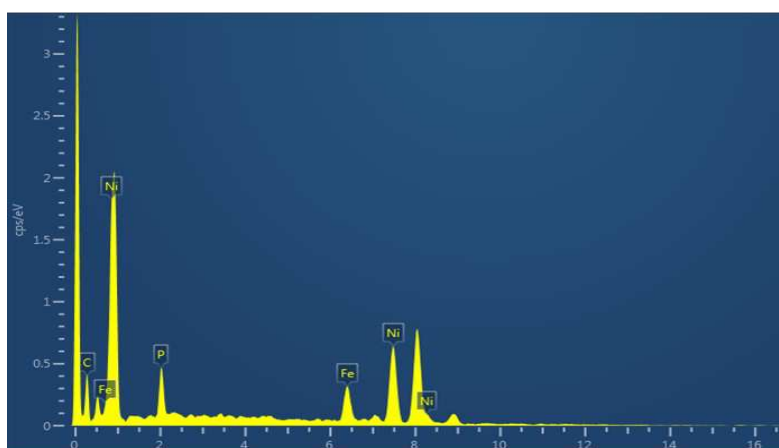


Figure 5: EDS Spectrum of Electroless Ni –P-CNT Coating.

3.3 Surface Roughness

Roughness of the substrate data was illustrated in table 4, as-plated and annealed. As mentioned above, increase in CNTs concentration to 0.4g/L causes a significant rise in the roughness. The roughness of sample Ni-P-0.4g/L CNT was higher in comparison with other specimens because large concentration of CNT which may produce agglomeration.

Table 3: Result of Surface Roughness Samples

Sample	Ra(μ)
Substrate	0.3
Ni-Pa plated	0.1
Ni-P-0.1 g/L CNT a plated	0.17
Ni-P-0.2 g/L CNT a plated	0.25
Ni-P-0.4 g/L CNT a plated	0.3
Ni-P a annealed	0.15
Ni-P-0.1 g/L CNT a annealed	0.2
Ni-P-0.2 g/L CNT a annealed	0.3
Ni-P-0.4 g/L CNT a annealed	0.4

3.4 Micro Hardness

Figure 6 shows the surface of microhardness samples of heat treatment. As noted, the CNTs reinforcing ability have force in enhancing the microhardness of surface, particularly in the sample of Ni-P-0.1 g/L CNT sample. These can be related with reinforcement and uniform distribution of carbon nanotubes about this specimen. The hardness of Ni-P-0.2 g/L CNT and Ni-P-0.4 g/L CNT was less when compared with the specimen having 0.1 g/L CNT due to the large CNTs concentration. In addition to that, segregation happened at the composite, which led to a decrease in the composite

microhardness of coated layer 18. However, the hardness of the heat-treated coatings of Ni-P was significantly increased. For example, it was about 2.8 times with respect to the corresponding value of the uncoated steel. However, the coating itself is an effective technique to achieve this goal, whether using Ni-P only or incorporating with CNT particle. However, the reasons behind such an increase in hardness appear to be different before and after heat treatment. P. Gadhari et al. (2014)¹⁹ pointed out that the microhardness of annealed composite coatings depends on three factors – level of incorporation of particles, annealing temperature and uniform distribution with less agglomeration of particles. For instance, the enhancement of hardness of Ni-P coatings when the deposition process variables remain; the nature of the coating layer only features and defines the extent of protection that can be provided by the coating.

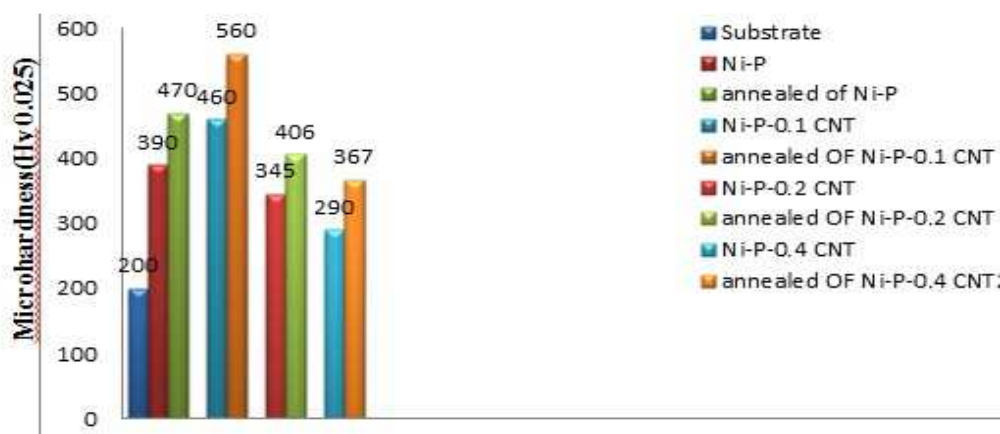


Figure 6: Microhardness Results of as-Plated and Heat Treatment of Samples Surface.

3.5 Wear Behavior

Figure 7(b) expresses planner for coefficient of the friction for samples plated. A substantial variation for coefficient of the friction was showed at sample Ni-P and these are related by a large mutual solubility of nickel and iron, which can cause an increment in the region of the surface contact coated with counterpart and high elimination for material. A further explanation for that behavior and crystallization of an amorphous-plated specimen through test of the wear because of heat generation, which is produced at the appearance of tensile stresses at the interface of crystalline and amorphous phases.^{20, 21}

Friction coefficient was decrement with elevation by CNT concentration of 0.1 g/L, so shear of lubricating film of carbon may be too easy, which decreases direct contact among counterpart and surface of samples in Figure 7(c) as [22]. Additional effects on behavior of wear of samples are roughness of surface. The larger surface roughness can lead to abrasive interactions among the roughness on surface sample Ni-P-0.4g/L CNT and counterpart to be conquered.

In fact, higher wear rate and friction coefficient result from lesser contact area that causes higher local pressure between the surface and pin of the specimen.

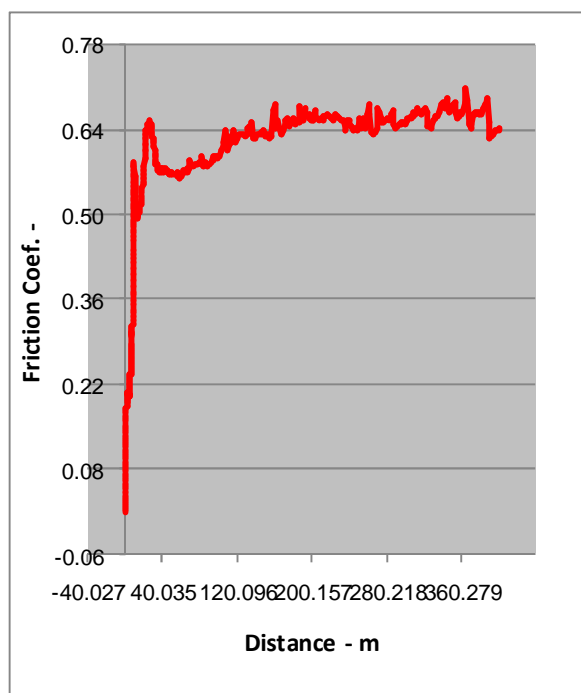
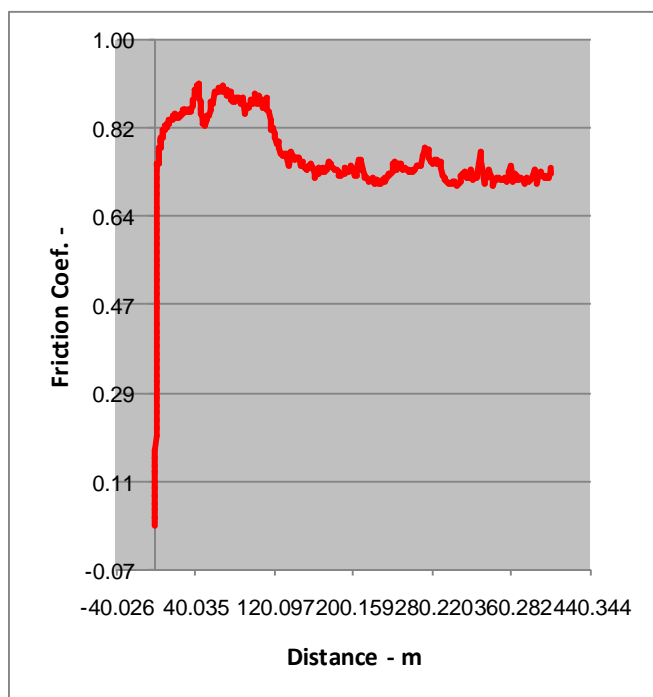
Figures 7(d) and (e) illustrate diagrams of the coefficient of friction of heat treatment specimen. Following heat treatment for Ni-P sample, there was clear decrement of friction coefficient al. The reasons for this result were high microhardness value that needed lower solubility of iron particles and more force of friction for plastic deformation. Ni-P contains CNT specimens like a decrement direction for coefficient of friction, which was seen following heat treatment. This behavior results from many causes; firstly, the microhardness value increment with the grain refinement. Secondly, through the electroless deposition process, the CNT is filled with surface microholes, which represent the sites of active tensile stress. Consequently, CNT can avoid speed of plastic deformation. Thirdly, CNT represented a main barrier to the

motion of dislocations when increment concentration of CNT to 0.1g/l causes an improvement in wear resistance properties and higher reduction in the friction coefficient. In addition, also CNT can help keep hold of composite hardness at large temperatures, which is a significant factor because of the heat generation through the wear test.

Table 4 illustrated mean of friction coefficient, rate of specific wear mass loss of as-coated and heat treatment. Therefore, friction coefficient can be noted and has a relatively direct rate of the specific wear. Also noted, the heat treatment Ni-P-0.1 g/l CNT has lesser rate of specific wear in contrast to other specimens because of some specific reasons like larger microhardness, smaller grain size, lesser coefficient of friction and most importantly homogenous distribution of particles. Wear rate decreases with increasing microhardness and formation of hard phases following the treatments as well as the low mutual solubility between iron and those phases, which could be responsible for increasing the wear resistance.²³ Severe removal of as-deposited coating occurred during the wear test. Since nickel and iron have high solubility in each other, adhesive wear can be considered as a predominant wear mechanism, while low mutual solubility between iron and Ni₃P phases results in abrasive wear.

Table 4: The Results Average Coefficient of Friction and Wear Rate of Coated Samples

Sample	Loss Weight*10 ⁻³	Coefficient of Friction	Specific Wear Rate (mm ³ /N.m) _x 10 ⁻⁴
Substrate	5.6	0.73	1.4
(Ni-P)a plated	2.7	0.64	0.68
(Ni-P-0.1 g/l CNT) a plated	1.5	0.61	0.38
(Ni-P-0.2 g/l CNT) a plated	2.2	0.62	0.55
(Ni-P-0.4 g/l CNT).a plated	2.7	0.64	0.68
(Ni-P) annealed	1.5	0.61	0.15
(Ni-P-0.1 g/l CNT) a annealed	0.9	0.54	0.2
(Ni-P-0.2 g/l CNT) a annealed	1.2	0.6	0.3
(Ni-P-0.4 g/l CNT) a annealed	1.5	0.63	0.38



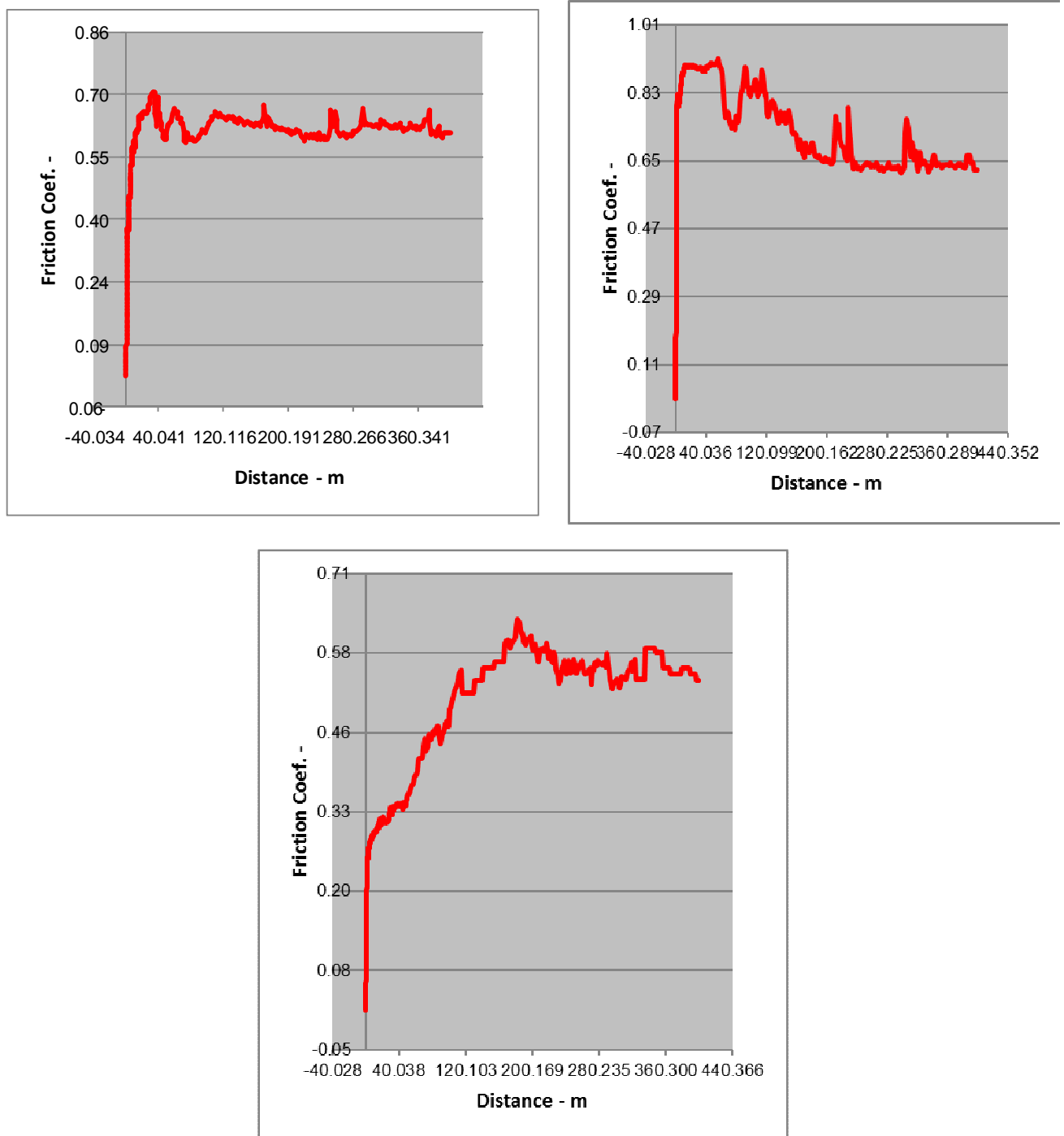


Figure 7: The Friction Coefficient Differences Versus Distance (a) as-Substrate, (b) Ni-P (Before Heat Treatment), (c) Ni-P-0.1 g/L (Before Heat Treatment), (d) Ni-P (After Heat Treatment), (e) Ni-P-0.1 g/L (After Heat Treatment).

4. CONCLUSIONS

- Coating low carbon steel with Ni-P increases the microhardness from (200 HV) to (470 HV) after heat treatment.
- Incorporation of both CNT particles in Ni-P coating layers increased microhardness (Ni-P-0.1 CNT) to 460 HV and 560 HV after heat treatment.

- After heat treatment, however, the weight lost was almost zero through wear test.
- No flaws were observed in the coating layers after heat treatment.

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